THE ELASTIC MODULUS OF NANO-SIZED ZINC DETERMINED BY LASER ULTRASONIC METHOD

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INTRODUCTION

The nano – sized materials are the advanced materials developed in the eighties[1] and being called nanocrystalline materials, ultra – fine grained materials or nanophase materials. Because there are a lot of interfaces within the nano – scaled materials, the volume fraction occupied by the interface is comparable with that of particles. The particle size effect and disordering effect of interface exist in the materials. They are referred to have "gaslike" structure. So the nano – sized materials have a number of advantages excelling to the traditional materials properties. Many new phenomena have been discovered from the investigations of their optical and electric properties. However few works are related to their mechanical and ultrasonic properties.

Laser ultrasonic method is an useful technology for characterizing materials since they have advantages of broad bandwidth of frequency, localization and noncontact measurement. It is suitable for the measurement of sample with small size and arbitrary shape. This technique has been used to study the ultrasonic velocities and attenuation of longitudinal (L –) wave for nano – scaled Cu(nmCu), and nmAg by us. The experimental results show two phenomena: (a) Usually the velocities of nm – metals are dispersive and their values are lower than that of conventional metals, expect compacting pressure is higher enough. (b) The attenuations spectra of such materials are similar to that of Polymers, depending on the grain size and fabrication condition of samples.

In this paper, the first results of the ultrasonic velocities of longitudinal (L-) wave, transverse (T –) waves and elastic constants for nmZn determined by laser ultrasonic method are presented. The relationship between the experimental values and the conditions of samples, as well as comparisons with that of conventional Zn, are analyzed and discussed.

PRINCIPLE

Under the first order approximation we regard the nmZn as an isotropic material. The coordination axes of orthogonal and cylindrical system are shown in Fig. 1. The Z axis is perpendicular to the surface of the sample. X and Y axes lay in the surface of sample. r and θ

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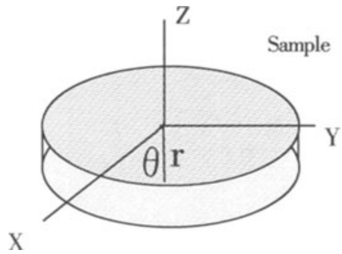

Fig. 1 Schematic diagram of the principle.

are its polar coordination. θ is a deviation angle of r deviating from the X axis. A laser beam irradiates the surface of sample at the origin point. As shown by the general stiffness matrix [c] of an isotropic solid, it has two independent elastic constants C_{11} and C_{44}. To guarantee the general elastic isotropy condition $C_{12} = C_{11} - 2C_{44}$ is required to be invariance of [c] for rotation about the Z and Y axes. These two independent elastic constants are often taken to be the Lame constants λ and μ defined by

$$\lambda = C_{12} \quad \text{and} \quad \mu = C_{44} \tag{1}$$

The propagation characteristics of plane wave in an isotropic solid may be found by the Christoffel equation expressed as [4]

$$[k^2 \Gamma_{ij} - \rho\omega^2\delta_{ij}][V_j] = 0 \tag{2}$$

where Γ_{ij} is called the Christoffel matrix. A dispersion relation is then obtained by setting the characteristic determinant of Eq. (2) equal to zero

$$\Omega\,(\omega, k_x, k_y, k_z) = [k^2\,\Gamma_{ij}\,(l_x, l_y, l_z) - \delta_{ij}\,\rho\omega^2] = 0 \tag{3}$$

where k is the wave vector, l_x, l_y, and l_z are its direction cosine with respect to the axes, ρ the density of material, V_j $(j = x, y, z)$ the vibration velocities of particles, ω the angle frequency of ultrasound, δ_{ij} the kronecker delta. ($\delta_{ij} = 1$ when $i = j$, $\delta_{ij} = 0$ when $i \neq j$). Γ_{ij} for an isotropic solid is given by:

$$[\Gamma_{ij}] = \begin{vmatrix} C_{11}\,l_x^{\,2} + C_{44}(1 - l_x^{\,2}) & (C_{11} + C_{44})l_x l_y & (C_{12} + C_{44})l_x l_z \\ (C_{12} + C_{44})l_y l_x & C_{11}l_y^{\,2} + C_{44}(1 - l_y^{\,2}) & (C_{12} + C_{44})l_y l_z \\ (C_{12} + C_{44})l_z l_x & (C_{12} + C_{44})l_z l_y & C_{11}l_z^{\,2} + C_{44}(1 - l_z^{\,2}) \end{vmatrix}$$

$$C_{12} = C_{11} - 2C_{44} \tag{4}$$

Which can be found in Ref. 4. Now let the $l_x = l_y = 0$, and $l_z = 1$, then Eq. (3) is separated into the three independent dispersive equations for X – and Y – polarized Z propagation transverse waves and the comporession wave respectively. The two equations of them for T – wave are the same.

$$k_t^{\,2}\,C_{44} = \rho\omega^2 \tag{5}$$

$$k_l^{\,2}\,C_{11} = \rho\omega^2 \tag{6}$$

Where ω/k_t and ω/k_l are the phase velocities v_t and v_l for the T – and L – waves respectively. Once the values of phase velocity of medium are known, the elastic constants can be estimated, vice versa. Then according to the elastic theory for an isotropic solid, the relation between the Young's modulus E, shear modulus G and Poisson's ratio ν are given by

$$\nu = \frac{\left(\frac{v_l^2}{2v_t^2} - 1\right)}{\left(\frac{v_l^2}{v_t^2} - 1\right)}, \qquad G = \mu \quad \text{and} \qquad E = 2\mu(1+\nu) \tag{7}$$

Usually, the signal of laser ultrasonic pulse is composed of the signals of waves with the different frequencies. The velocity of nm material is dispersive especially at the region of lower frequency. The Eq.(5) to (7) can be used while the phase velocity for fixed frequency has obtained by a phase spectrum method.

EXPERIMENT

Three kinds nmZn wafers composed of super fine particles with size of 60, 110 and 120 nano – meter(nm) are used as the samples here. The powders of nmZn with different grain size are produced using the high frequency heating and gas evaporation method in inert atmosphere at room temperature. Then the sample wafer is made by compacting these nmZn powder. The wafers have 10 mm in diameter and 0.64 to 3.84 mm in thickness respectively. The parameters of nmZn, such as its density ρ, grain size S, thickness h and porosity P_0 are shown in Table 1.

The experimental system used is given by Fig.2, which is similar to that shown in references [2-3]. It is established by us. A Nd:YAG laser beam is focused into a spot with slightly larger than 3 mm in diameter. It enable the ultrasonic wave to be approximately regarded as a plane wave propagating in the sample. The Nd:YAG Q – switched laser with duration 8 ns, adjustable pulse energy from 1μJ to 10 mJ and repetition frequency of 10Hz is used as an excitation source. A PVDF transducer coupled by water and two kinds of shear wave transducers coupled by phenyl solicylotesy are used as receivers. The PVDF transducer with frequency bandwidth of 125 MHz is used to detecte of L – wave. One $LiNbO_3$ shear wave transducer with center frequency f_0 of 7.5 MHz and one PZT transducer with center frequency 400KHz are used to detect the T – wave respectively. The signal of ultrasonic pulse received by PVDF or PZT transducer is fed into a digitized oscilloscope (HP54510B), which has sampling ratio up to 1Gbits/S. Then the signal is processed by computer. So the waveform of the L – wave and T – wave propagating back and forth in the sample can be obtained. The propagating time t_l and t_t of (L-) and (T-) waves are measured and used to determine the velocities v_l, v_t and the elastic constants. The elastic engineering modules (Possion's ratio ν, Young's module E and shear module G) can be calculated using the velocities, and elastic constants respectively.

The experimetal waveforms for three kinds of samples are shown in Fig.3 to Fig.5. Fig.3 shows the L – waves waveforms received by PVDF transducer (a) for Z26A – 3, (b) for Z27B and (c) for Z28B samples, respectively. Fig.4 shows the T – wave waveforms received by $LiNbO_3$ transducers. Fig.5 shows the T – wave waveforms received by PZT transducers. In Fig.4 and Fig.5 the waveforms in (a) (b) and (c) are detected for samples of Z26A – 3, Z27B and Z28B respectively.

Table 1 Parameters of samples.

Sampl	nmZn Z26A-1 #	nmZn Z26A-2 #	nmZn Z26A-3 #	nmZn Z	nmZn Z28B #	Zn
ρ(kg/m^3)	3730	3260	3730	3210	3400	6900
h(cm)	0.384	0.2	0.064	0.0740	0.064	
S(nm)	110	110	110	120	60	
Porosity P_0%	45.94	52.75	45.94	53.48	50.72	0

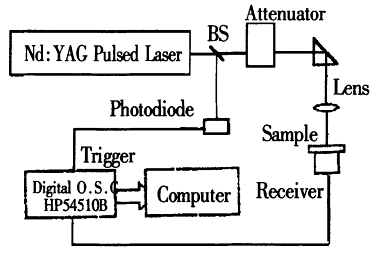

Fig.2 The experimental system.

ANALYSIS

From Fig.3, we can see clearly the directly arriving pulse signal and the first as well as the second echoes. Thus the time t_l of L – waves propagating back and forth in the sample can be measutred from these waveforms. From Fig.4 and Fig.5, the directly arriving ultrasonic pulses and echoes can not be clearly distinguished, because the band width of frequency of receiver are too narrow. So the propagating times t_t of T – wave pulse are obtained by making the comparison of the time of flight t_s of the wave passing through the sample and transducer with a standard time of flight t_0 ($t_t = t_s - t_0$). The standard t_0 is the delay time of the transducer. As done in the pulse echo and time of flight methods the velocities are calculated by using the following equations.

$$v_l = \frac{2h}{t_l} \tag{8}$$

for pulse echo method and

$$v_t = \frac{h}{t_t} \tag{9}$$

for time of flight method. For L – wave signal with broadband width of frequency, the analysis of the waveform may determine the group velocity, the phase velocity spectrum. The attenuation spectrum for the sample may obtained by using the phase spectrum method[5]. We get the phase spectra and amplitude spectra of the directly arriving pulse and its first echo by FFT. Then the phase velocity spectrum can be calculated using the phase spectra according to the equation (10). The attenuation spectrum can be calculated using the amplitude spectra according to the equation (11).

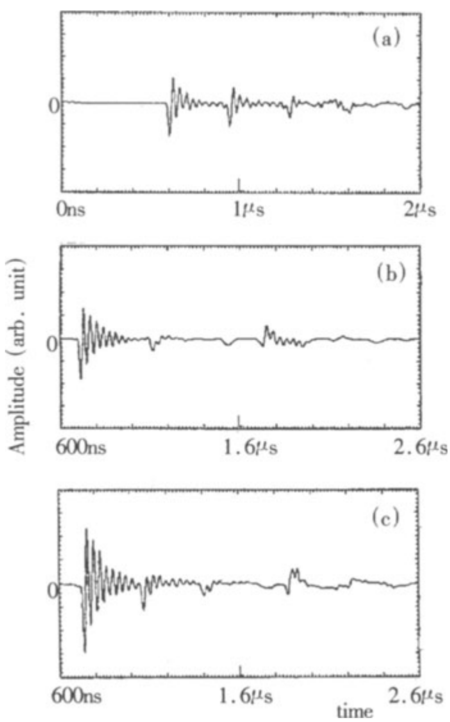

Fig.3 The waveforms of L – waves, (a) for sample Z26A, (b) for sample Z27B and (c) for sample Z28B respectively, received by PVDF

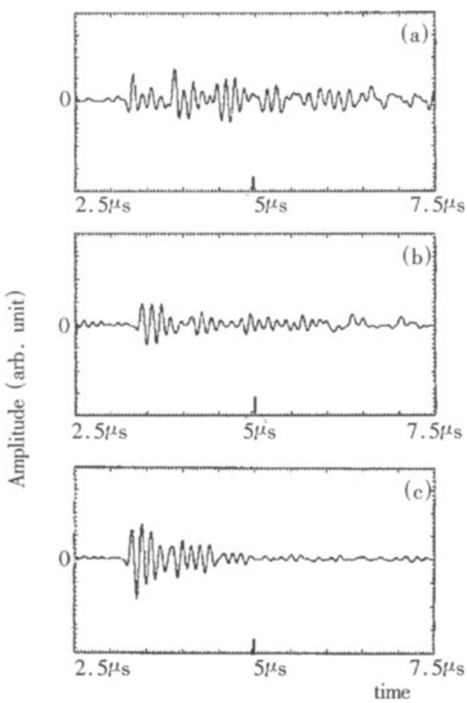

Fig.4 The waveforms of T – waves, (a) for sample Z26A, (b) for sample Z27B and (c) for sample Z28B respectively, received by $LiNbO_3$ transducer with center frequency of 7.5 MHz.

$$v(\alpha) = \frac{\omega(z_1 - z_2)}{\varphi_1(\omega) - \varphi_2(\omega) + 2m\pi} \tag{10}$$

$$\alpha(\omega) = \frac{1}{2h} \ln \frac{|F[u(z_1,t)]|}{|F[u(z_2,t)]|} \tag{11}$$

Where v and α are the phase velocity and attenuation of L - wave respectively, ω is the angle frequency, φ the spectrum of phase, F the frequency spectrum and u the displacement signal of longitudinal wave. z_1 and z_2 are the positions of propagation distances. As an example, the spectra of amplitude and phase velocity obtained by FFT for a sample Z27B are shown in Fig.6. In the Fig.6, (a) and (c) show the spectra of amplitudes for the directly arriving pulsed signal and for its first echo respectively, (b) and (d) show the spectra of phase for that signals respectively. The calculated spectra of velocities and attenuation for three kinds of samples are shown in Fig.7 and Fig.8. The curves illustrate that the phase velocities and attenuations are dependent on the frequency and the properties of samples. It can be fitted by the following equations:

$$\begin{aligned} \alpha(f) &= 2.68 + 5.33f - 0.33f^2 + 0.07f^3 \pm O(f) \\ v(f) &= 232.59 + 24.92f - 1.43f^2 + 0.038f^3 \pm O(f) \end{aligned} \tag{12}$$

for sample Z26A, where f is the frequency of ultrasonic wave.

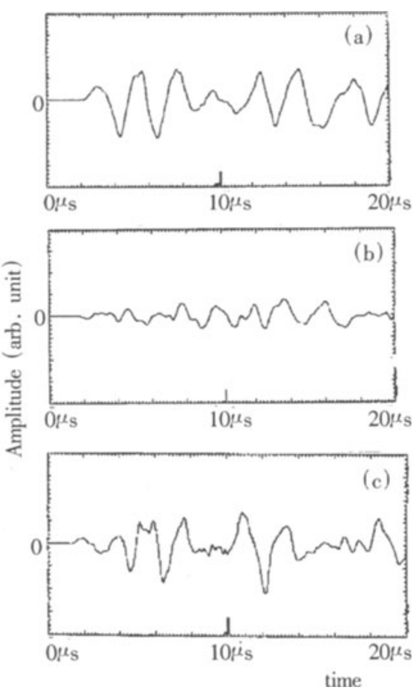

Fig.5 The waveforms of L - waves, (a) for sample Z26A, (b) for sample Z27B and (c) for sample Z28B respectively, received by PZT transducer with center frequency 400KHz.

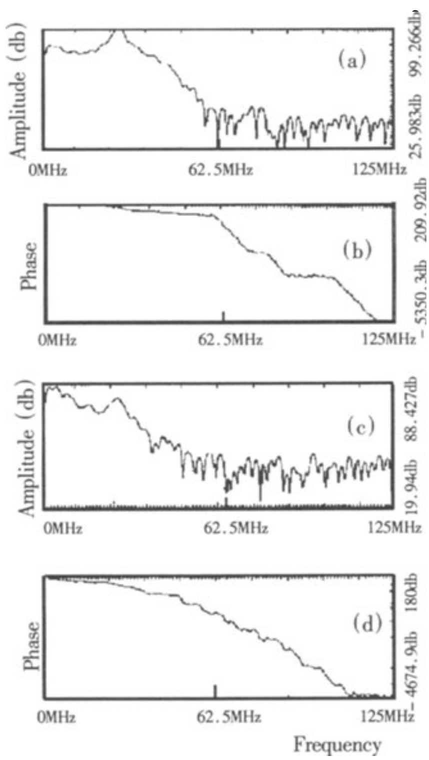

Fig.6 The spectra of the signals straight arrived and its first echo, (a) and (c) are the amplitude spectra, (b) and (d) are the phase spectra respectively.

$$\alpha(f) = 37 + 3.15f + 0.17f^2 - 0.002f^3 \pm O(f)$$

$$v(f) = 304 + 0.088\,f \tag{13}$$

for sample Z27B, and

$$\begin{aligned} \alpha(f) &= 7 + 4.35\,f - 0.2\,f^2 + 0.006\,f^3 \pm O(f) \\ v(f) &= 0.024f + 376.52 \end{aligned} \tag{14}$$

for sample Z28B. Where O(f) denotes the value can be omitted. These fitted equations explain that the first - power frequency dependence is dominated. Fig. 9 shows the comparison between the velocity spectra and attenuation spectra for three kinds of nmZn samples,

The elastic constants, modulus and Poison's ratios of these nmZn samples are deduced from the ultrasonic velocities measured and based on the relation between the velocities and elastic modulus for an isotropic solid (cf Eq. (5) to (7)). The elastic constants deduced also obviously depend on frequency. The values of experimental and calculated results, including the velocities for frequency 7.5 MHz and 400KHz as well as the elastic constants are listed in

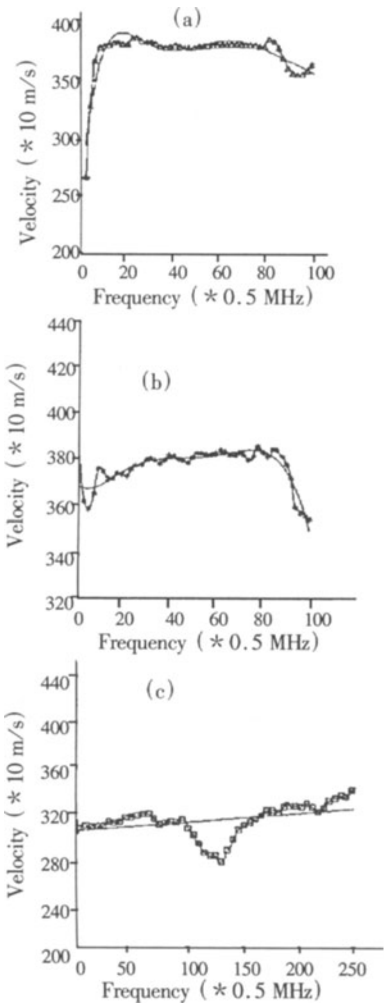

Fig. 7 The velocity spectra for nmZn, (a) for Zn26A, (b) for Zn28B and (c) for Zn27B respectively.

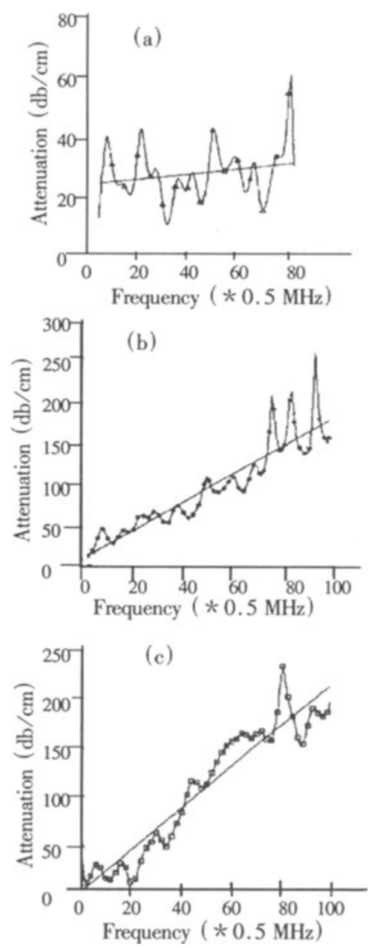

Fig. 8 The attenuation spectra for nmZn, (a) for Zn26A, (b) for Zn28B and (c) for Zn27B respectively.

Table 2. The velues of engineering elastic modules are listed in Table 3.

From Table 2 and 3, it can be seen that: For the samples here used, the velocities are dependent on the parameters of samples and the frequency of ultransound especially at the lower frequency region. The values of transverse waves velocities are from 941 to 1587 m/s and that of the L – waves are from 2133 to 2408 respectively. The value of Poison's ratio is from – 0.31 to 0.22 for frequency of 7.5 MHz. The velocities and elastic constants of the nmZn are lower than that of the conventional Zn.

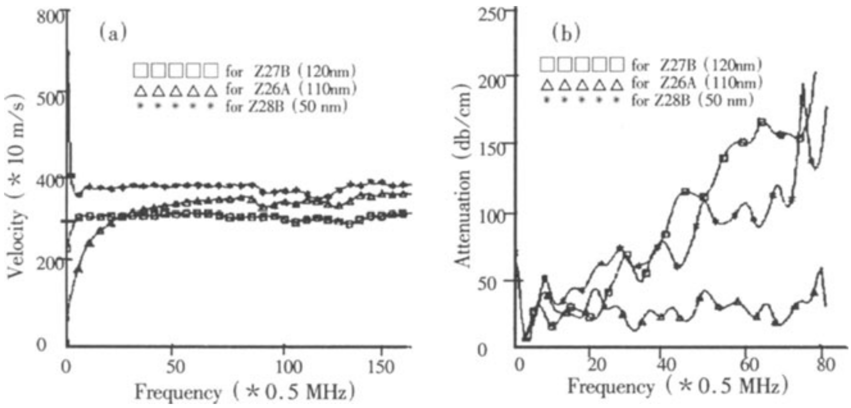

Fig. 9 The comparison between the velocity spectra and attenuation spectra for three kinds of nmZn samples, (a) is for the velocity spectra and (b) is for the attenuation spectra.

Table 2 The experimental results of ultrasonic velocitics and elastic constants of nmZn samples and conventional metal Zn.

Sample	nmZn z26A 1 #	nmZn z26A 2 #	nmZn Z26A 3 #	nmZn Z27B #	nmZn Z28B #	Zn
t_l (ns)	2030	1040	338	400	332	
t_l (7.5MHz)	1720	950	300	410	270	
t_t (400KHz)		1026	680	680	520	
V_l (m/s)	3780	3846	3810	3700	3855	4170
V_t (7.5MHz) (m/s)	2232	2105	2133	1850	2370	2408
V_t (400KHz) (m/s)		1587	941	1088	1230	2408
V_l (7.5MHz) (m/s)			2710	3074	3728	4170
C_{11} ($*\ 10^{10}N/m^2$)	5.29	4.82	5.41	4.39	5.05	12
C_{11} (7.5MHz) ($*\ 10^{10}N/m^2$)			2.73	3.03	4.73	
C_{44} (7.5MHz) ($*\ 10^{9}N/m^2$)	18.58	14.45	16.97	10.99	19.10	40
C44 (400KHz) ($*\ 10^{9}$N/m2)		8.21	3.30	3.70	5.14	

Table 3 The engineering elastic modulii of nmZn samples and conventional metal Zn

Samples \ modules	G(400KHz) (* $10^9N/m^2$)	G(7.5MHz) (* $10^9N/m^2$)	λ(7.5MHz) (* $10^9N/m^2$)	E(7.5MHz) (* $10^9N/m^2$)	ν (7.5MHz)
nmZn Z26A 3 #	8.21	16.97	- 6.6	- 45	- 0.31
nmZn Z27B #	3.30	10.99	8.36	22.45	0.22
nmZn Z28B #	3.70	19.10	8.8	44.35	0.16
Zn	40	40	40	100	0.25

CONCLUSIONS

From the mentioned above, some conclusions can be obtained as follows:

1. The laser ultrasonic method is an useful tool for investigation of acoustic properties and determination of elastic constants of nm material with smaller size and thin thickness.
2. The velocities and the attenuations of nmZn samples used in our experimens are related to grain size of the sample and frequency of laser ultrasound.
3. The velocities are lower than that of conventional metal Zn(Zn). When the grain size of nmZn is changed from 60 nm to 120 nm, the velocity of L - wave is about 7.6% to 11.3% lower than that of Zn for the higher frequency, and about 10.6% to 35% at frequency of 7.5MHz.
4. The velocity of T - wave is about 1.65 to 23.2% lower at frequency of 7.5 MHz and bout 34% to 61% at the frequency equal to 400KHz. The larger the grain size of the sample, the lower is its velocity.
5. The elastic modules are lower than that of Zn and dependent on the frequency. The lower the frequency, the lower is elastic module. In addition, the elastic module soft effect may appear for some frequency (cf Fig 7(c)).
6. The attenuation spectra for three kinds of nmZn are dependent on the frequency,and the first - power frequency dependence is dominated, while the attenuation to frecquency is square dependence for Zn in normal case .

The further investigations on the relation between the elastic modules and frequency for nano - materials are needed and they can be done in the near future.

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